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(54) Preparation of alcohols from olefins having from 3 to 7 carbon atoms.

(57) The process comprises conducting an oxo reaction with
olefins having from 3 to 7 carbon atoms to obtain aldehydes
having from 4 to 8 carbon atoms and containing at least 50%
 α -aldehydoalkanes, and subjecting the aldehydes to an aldol
reaction to convert the aldehydes to aldol product but with
that produced from cross-aldolization of 2-substituted
aldehydes constituting no more than 20% of the product, and
hydrogenating to obtain alcohols.

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PREPARATION OF ALCOHOLS FROM OLEFINS

HAVING FROM 3 TO 7 CARBON ATOMS

The present invention is concerned with preparing alcohols from olefin feedstock.

5 The present invention is further concerned with preparing ten-carbon plasticizer alcohols from substantially linear butene feedstock.

Background of the Invention

Various lower olefinic stocks are available
10 from petroleum sources, and many procedures are known for converting lower olefins to high olefins, or to higher molecular weight compounds with various functional groups. Among such procedures are catalytic dimerization procedures for converting propylene and butenes to heptenes and
15 octenes respectively and such dimers can be catalitically hydroformylated to aldehydes, which can be reduced to alcohols. Lower olefins can be hydroformylated, using rhodium, cobalt, or
20 other catalysts, to the corresponding aldehydes. Aldehydes in turn can be converted to higher aldehydes by the well known aldol reaction, such

as that taught in U.S. Patent 2,921,089 for converting n-valeraldehyde to 2-propyl-2-heptanol, and then hydrogenated to 2-propylheptanal and 2-propylheptanol. It is also known that various 5 alcohols can be utilized to esterify phthalic acid to form useful plasticizers, e.g. 2-ethylhexanol, 2-propylheptyl alcohol, decyl alcohols, etc. as disclosed in the aforesaid 2,921,089. It is also known to conduct an aldol reaction of mixtures 10 of normal and branched aldehydes under conditions which force cross aldol reaction of the branched aldehyde with the normal aldehyde, see U.S. Patent 2,852,563.

15 Among dimerization processes is the Dimersol[®] dimerization process for dimerizing olefins using a nickel coordination complex and an aluminum alkyl as catalyst. The process can convert propylene to hexenes with selectivity in excess of 85%. 20 The hexenes can be converted by oxo reaction to aldehydes and then alcohols, producing heptanols. M. Johnson has studied oxo reaction of 4-methylpen-1-ene, showing migration of the double bond during the reaction, and fairly large production of a 25 2-substituted aldehyde, 2,4-dimethylpentanal, along with 5 methyl-hexanol as the main product (J. Chem. Soc. 1963, 4859).

Reactions of the type described characteristically produce mixtures of isomeric products. Therefore in the production of plasticizer alcohols, distillations may be employed at an early stage to separate isomeric materials. An alternative is to effect selective reaction of the isomeric materials with resulting effect upon product properties.

Summary of the Invention

The present invention involves a process in which mixed butenes are converted to a ten-carbon plasticizer alcohol comprised of at least about 80-90% 2-propylheptanol by an oxo reaction of the butenes to obtain amyl aldehydes with at least about 66% n-pentanaldehyde content, followed by an aldol reaction of the aldehydes under conditions to cause substantially all of the n-pentanaldehyde to react but with incomplete conversion of branched aldehydes, and then hydrogenating to produce alcohols in which the ten-carbon alcohols are comprised of at least 80-90% 2-propylheptanol. Under the aldol conditions employed the 2-methylbutanal present does not readily condense with itself, and condenses at a comparatively slow rate with the n-pentanal, so that the 2-propyl-4-methylhexanol content (resulting from the so-called cross aldol of n-pentanal with 2-methylbutanal) in the resulting alcohol is held to no more than about 15-20%, often 12% or less. The ten-carbon alcohol mixture, after isolation from other components, is admirably suited as a plasticizer alcohol, having good plasticizing properties as the phthalate diester. It approaches the excellent plasticizer properties of the 2-propylheptyl phthalate, as the small amount of 2-propyl-4-methylhexanol causes only a slight decline in such properties.

5 The described procedure is advantageous in that it avoids the expense of a fractionation of difficultly separable aldehyde isomers prior to the aldol reaction, and produces an excellent plasticizer alcohol in high yield by an efficient procedure from the source materials. The main side product, 2-methylbutanol, is in itself useful as a plasticizer alcohol. The invention utilizes selective aldol reaction as a step in producing
10 a quality plasticizer alcohol without normally requiring separation of aldehyde isomers prior to aldol condensation. This contrasts with the procedure used in 2-ethylhexanal manufacture in which propylene is hydroformylated to a mixture of n-butanal
15 and 2-methylpropanal (isobutyraldehyde), and the mixture of close boiling isomers is then carefully separated by fractional distillation in an expensive multiple tray column, so that the n-butanal can be taken forward to an aldol reaction.

20 The invention is further concerned with process in which olefins selected from those with 3 to 7 carbon atoms are converted to aldehydes with 4 to 8 carbon atoms, which are then subjected to aldol condensation to obtain aldol products in
25 relatively high yield for hydrogenation to alcohols having useful properties and derivative uses, with especial interest in conversion of hexenes to heptanals and to C₁₄ alcohols for use in detergents.

Under the aldol conditions employed, the n-pentanal reacts with itself to form aldol product at a rate about 15 times greater than it reacts with 2-methylbutanal. The aldol reaction is permitted to go to 80% or so completion so that if about 25% of the aldehyde supplied is 2-methylbutanal, about 3/4 of it will remain unreacted, and about 28% of the aldol product will be that from self-condensation of n-pentanal. The conversion of n-pentanal to aldol product will be very high and desirably nearly complete, such as upwards of 90 or 95%. There will be some variation with conditions and isomer content of the aldehydes utilized, but the present invention contemplates obtaining aldol product with about 80% to about 95% being from the self-condensation of n-pentanal, and preferably at least 85% from self-condensation with no more than 15% of 2-propyl-4-methylhexanal being produced. In the present process, the aldol intermediate, 2-propyl-3-hydroxyl-heptanal will ordinarily be dehydrated in the aldol procedure to 2-propylheptenal. Under some conditions the immediate aldol product can be isolated, but ordinarily under the temperature conditions employed herein the 2-propyl-2-heptanal is produced. The aldol reaction can utilize strongly alkaline catalyst, such as sodium and potassium hydroxide, or sodium and potassium cyanide. The concentration of the aqueous alkali can be varied, but molar or similar concentrations of alkali metal hydroxides can be used, and concentrations selected will generally be in the range of about 1 to 10% by weight. The amount of aqueous alkali to aldehyde reactant can also vary, for example from about 15%

The present invention in one particular aspect employs an oxo reaction of butenes to obtain a mixture of aldehydes, which is then subjected to an aldol reaction. The oxo reaction involves 5 contacting substantially linear butenes with hydrogen and carbon monoxide and hydroformylation catalyst under hydroformylation conditions suited to obtaining a high proportion of n-pentanal in the aldehyde product. It is desirable to have 10 the n-pentanal to branched aldehyde ratio at least about 2.0:1, representing at least about 66.7% n-pentanal content. Aldehydes with 70-75% normal content, or even higher normal contents are desirable to the extent available from oxo, 15 reactions, possibly up to 85%, and will be useful for the aldol stage of the present invention.

The aldol reaction is carried out utilizing the usual aldol catalysts and conditions to promote the aldol reaction of the n-pentanal, using 20 elevated temperatures upwards of 60°C., particularly temperatures of about 90°C. to 130°C., or possibly up to 150°C. or higher if desired. The reaction is operable over broad pressure ranges including pressures less than atmospheric as well 25 as elevated pressures, but will usually be effected at slightly elevated pressures sufficient to maintain the reactants substantially in the liquid state. The reaction can also conveniently be conducted at reflux. The conditions and parameters discussed 30 and illustrated herein with respect to butenes and pentanals are in general exemplary of those for other olefins and aldehydes.

is from 1/3 to 1/2 of the mixture; and, of course, higher proportions of 1-butene could be used if available, up to 100% 1-butene. It happens, however, that the amount of normal aldehyde product is not 5 very sensitive to increases in the 1-butene content in ranges above 50%.

It is important that the hydroformylation of the mixed linear butenes gives a relatively high ratio of normal aldehydes, as this contributes to 10 the feasibility of using the aldehyde mixture for an aldol reaction to obtain a fairly high yield of 2-propylheptanal (and ultimately 2-propylheptanol) without excessive 2-propyl-4-methylhexanal. The use of moderate temperatures in the hydroformylation 15 contributes to obtaining about a 3:1 mixture of normal to branched aldehyde. Thus temperatures sufficient to produce an appreciable reaction rate, ranging from 80° to 100°C. or so can be used, and temperatures on up to 125 - 130°C. can be employed 20 to obtain better reaction rates. Still higher temperatures up to 150°C. or higher can be used but with a tendency to produce more branched aldehyde than desired. To some extent high catalyst 25 concentrations can be employed to obtain reaction rates, even at relatively low temperatures. Cobalt catalyst is especially suited to obtain the desired high proportion of normal aldehyde. Unmodified cobalt carbonyl catalyst can conveniently be used. Such catalyst, conventionally designated as cobalt 30 octacarbonyl, can be provided or employed in many forms known to be useful as a hydroformylation catalyst, although it may be necessary to exercise

by volume aqueous alkali up to about 75% by volume aqueous alkali. The aldol reaction will be run for a sufficient time to obtain the desired degree of conversion, which for batch reactions may be in 5 the range of about 1 to about 3 hours, while in continuous reaction times of less than five minutes are achievable. The reaction is stopped by permitting the reaction mixture to cool and separating the organic reaction phase from the aqueous alkali 10 phase. Since the n-pentanal reacts more rapidly than its isomers, the proportion of the isomers in the reacted aldehyde increases, and it therefore is not generally desirable to separate and recycle unreacted components to the reaction.

15 For the oxo reaction, linear butene streams are available which may have up to 70% 1-butene with the balance 2-butene. Butene streams generally contain isobutylene also, but the isobutylene can be separated in a reaction with methanol producing 20 methyl tertiary butyl ether, making linear butenes available which are substantially free of isobutylene. The hydroformylation procedures described herein can be employed to obtain aldehydes with a great predominance of the n-pentanal from linear butenes 25 containing even a high proportion of 2-butene, as even 2-butene itself produces a pentanal: 2-methylbutanal ratio of about 2.33, and a 1:2 mixture of 1-butene:2-butene produces product ratios in the range of about 2.8:1 to 3.1:1. In terms of available and effective materials, it may be desirable 30 to employ linear butene mixtures in which 1-butene

and the resulting heptaldehydes can be reacted in an aldol reaction to produce aldol products which can be hydrogenated to C₁₄ alcohols.

5 The described route to C₁₄ alcohols gives an alcohol having properties suitable for use in preparing detergents. While the alcohols have some branching, much of the product is mono-branched, or of a branched structure which can be biodegraded. Thus, depending upon particular procedures utilized, the product may be comprised in large part of 2-pentylnonanol, possibly with a small fraction of 2-pentyl-4-methyloctanol. Such structures, with non-adjacent branches, are susceptible to biodegradation.

15 For reactions where the ultimate product is a plasticizer, as usual in those involving aldol reactions of pentanals, there is interest in limiting cross-aldol reactions which increase chain branching. However, for other uses where branching 20 is not necessarily detrimental, some cross aldol reactions are useful as augmenting the efficient utilization of feed stock materials. Thus in a broader sense the present invention can utilize aldol reactions in which there is aldol and cross-25 aldol condensation of n-aldehydes along with branched aldehydes in which the branching is not at the 2-position, or generally including the class of alkanals except for those substituted on the 2-position. This applies to aldehydes with

some choice to provide catalyst best suited to obtaining a high proportion of normal product.

The oxo stage of the reaction can be conducted under the usual conditions pertaining to cobalt catalyzed hydroformylation reactions, with attention to the temperature conditions as described above. Usual pressure conditions apply, such as 6.89-27.56 MPa or up to 34.45 MPa total pressure, with most of the pressure being from the carbon monoxide and hydrogen supplied. The carbon monoxide and hydrogen are conveniently used in 1:1 ratio and obtained from usual synthesis gas sources, but other ratios can be employed in keeping with known hydroformylation practice. The reaction can be carried to the desired stage of completion in 1 to 3 hours or so on a batch basis, varying with time, temperature, pressure and catalyst concentration.

The reaction can be conveniently conducted either without a solvent or with solvents and, employing concentrations customary for homogeneous catalyst reactions, such as 2 to 10 molar or greater concentrations of the butenes in a solvent, e.g., hydrocarbon solvents such as toluene, and 0.1% to 1% by weight, based on cobalt, of catalyst.

The present invention is also concerned with preparing detergent range alcohols from propylene feedstock. The detergent range alcohols are somewhat higher in carbon number than plasticizer alcohols, often having about 14 carbon atoms, but in some cases ranging from about 11 to about 16 or so carbon atoms. Propylene can be dimerized to hexenes, and the hexenes can be converted to aldehydes by an oxo reaction as described herein,

5 aldehydes to be reacted does not become undesirably high. The 3-methylbutanal is more prone to react in the aldol reaction than the 2-methylbutanal isomer, so it is desirable to keep its presence to a minimum.

10 The hydrogenation of the enals from the aldol reaction can be conducted under the usual catalytic hydrogenation conditions for reducing olefinic bonds and aldehyde groups. The carbon-to-carbon bond reduces more rapidly and at a lower temperature than the aldehyde group, e.g. at about 90°C., with cobalt on Kieselguhr catalyst at elevated hydrogen pressure. The hydrogenation will generally be carried out at 3.45-13.8 MPa, or greater hydrogen 15 pressures and temperatures of 130° to 200°C. or higher, although any temperatures which are effective with a particular catalyst can be used. The stated conditions will be effective for reducing both the carbon-to-carbon bond and the aldehyde group 20 to obtain saturated alcohol. Various other hydrogenation catalysts can be used including platinum and platinum on carbon catalysts, copper chromite, activated nickel etc., and individual catalysts can be utilized in conjunction with other catalysts.

25 The present invention involves an oxo reaction, followed by an aldol reaction, and then a hydrogenation to convert enals to alcohols. For large scale operations, the oxo reaction will be conducted with usual provisions for separating gaseous 30 reactants and products, and catalyst, from the aldehyde products, with recycle as appropriate. The aldehyde product mixture will then be subjected to an aldol reaction, followed by decantation and water washing or other simple procedures to separate

4 to 8 carbon atoms, as obtainable from oxo reactions of C₃ to C₇ olefins, and applies particularly to aldehydes with 6 to 8 carbon atoms. Thus in such aldol reactions, crude oxo mixtures containing a number of isomers may be employed, and substantially complete reaction of all the aldehydes except the 2-substituted aldehydes can be achieved. For example, better than 95% conversion of α -aldehydo alkanes can be achieved, while conversion of 2-substituted aldehydes may be in the neighborhood of 25 to 30% or possibly even up to 50%. Thus it is feasible to use such crude oxo mixtures in aldol reactions to obtain useful products. Using oxo product in which the α -aldehyde alkane content may range from 60 up to near 80% or so, aldol conversions may approach 75 to 90%, even though participation of the 2-substituted aldehydes is limited, so that it is involved in cross-aldol producing no more than 20% of the product.

It is possible to obtain butene streams which are substantially linear and substantially free of isobutylene, in which no more than 2% or so of the butenes is isobutylene, and it is advantageous to use such butene streams. However, somewhat more isobutene can be tolerated, so long as the total of the resulting 3-methylbutanal together with other branched aldehydes in the

for some purpose, separation is appropriate, and this has the advantage of avoiding unnecessary hydrogen use.

5 Hexenes, as produced by dimerization of propylene with transition metal catalysts, as in the Dimer-sol[®] dimerization process, are characterized by being composed almost entirely of internal olefins, and a linear content generally reported as about 20%, but ranging up to 29% or so. The main isomer present
10 is a 2-methyl-2-pentene, along with other 2- and 4-methyl pentenes and around 6% 2,3-dimethyl-2-butene.

15 The linear hexenes can be separated from the crude dimerization product by use of a molecular sieve or other suitable procedure, and the linear hexenes alone then subjected to an oxo reaction to obtain heptanal products, with the linear content of the heptanals ranging up to 75% or more. Branched isomers which may be present include 2-methylhexanal, and 2-methylpentanal. The oxo product mixture
20 can be reacted in an aldol reaction, employing aldol conditions as described herein, to produce aldol products. Under the aldol conditions employed, the n-heptanal reacts with itself at a rate about 10-15 times faster than it reacts with 2-methylhexanal or other 2-substituted aldehydes. Thus, when the C₇ aldehydes are produced from linear hexenes, a product compound predominantly of product from self-condensation of n-heptanal can be obtained by carrying out an aldol reaction of the oxo reaction product, with some control over the amount of product from 2-substituted aldehydes by controlling the amounts of conversion which is permitted. It may be desirable to have better than
25
30

the organic product-containing phase from the aqueous phase. The product phase is then hydrogenated, converting both the C₅ aldehydes and C₁₀ enals to the corresponding alcohols. The hydrogenation is followed by a distillation to remove light ends, followed by a distillation to remove C₅ alcohols. Both the C₅ and C₁₀ alcohols can then be treated in further hydrogenation polishing operations to improve the alcohol quality by insuring complete hydrogenation. The ten-carbon alcohol mixture thus obtained will, as described herein, have a high content of 2-propylheptanol with only small amounts of 2-propyl-4-methylhexanol or other branched alcohols, the amounts of such materials being sufficiently small that the alcohol mixture has properties suitable for a plasticizer alcohol.

The five-carbon alcohol co-product obtained is principally 2-methylbutanol, a useful product; historically five-carbon alcohols have more value than ten-carbon alcohols. The separation of the five-carbon from ten-carbon alcohols is readily effected by distillation in equipment constructed of inexpensive alloys such as carbon steel. Separation at this stage is simple, compared to the difficult separation which would be required to separate the five-carbon aldehyde isomers prior to the aldol reaction.

As an alternate to the above procedure, it is possible to separate the five-carbon aldehydes by distillation from the 10-carbon enals prior to hydrogenation. For convenience of separation, distillation of the alcohols is generally preferred, and then the five-carbon components are in the form of alcohols. However, if the aldehydes are desired

operation will possibly range from 50 to 65%.

The C₇ branched aldehydes which do not react in the aldol reaction can be separated from the reaction mixture for various purposes, or hydrogenated with the mixture and utilized as a C₇ branched alcohol. If desired, the branched C₇ alcohol can be dehydrated, and then subjected to an oxo reaction to produce an aldehyde with an additional carbon atom. Thus 2-methyl-hexanol can be converted to 2-methylhexene-1, which can be recycled to the oxo stage of the reaction process and hydroformylated to predominantly 3-methyl-heptanal. This 3-methylheptanal, not having any substituent in the 2-position, reacts at a good rate in the aldol reaction. Other unreacted aldehydes, such as 2,4-dimethylpentanal and 2-ethyl-pentanal, can similarly be hydrogenated and dehydrated and recycled to be converted in the oxo stage to C₈ aldehydes with no substituent in the 2-position, which will take part in the aldol reaction when recycled through that stage. This procedure to use the unreacted C₇ aldehyde results in greater conversion of the original reactants to the desired final product, rather than to a concomitant product such as C₇ alcohols. Use of this recycle feature in the oxo-aldol process changes the product obtained from linear hexenes considerably, and can produce a product composed on a mole basis of about 40% 1-pentyl-nonanol, about 30% 2-pentyl-5-methyl-nonanol, and about 10% of 2-(1-methylpentyl)-5-methyl-nonanol.

50 or 60% completion for efficient use of feed stock, and conversions of 80% or higher may at times be desirable. The reaction can be run to achieve 95% or better conversion of the n-aldehyde to aldol product, while only about 1/4 to 1/3 or so of the 2-substituted aldehydes are usually converted to aldol product by a cross-aldol reaction. With use of appropriate control, aldol product with about 80% to say 95% from self-condensation of n-heptanal can be obtained, for example at least 85% from self-condensation, with no more than 15% of cross-aldol product. Depending upon the properties desired in the product, the degree of branching can be controlled to a considerable extent by the present process. It happens that some known detergent range alcohols have a fair degree of branching and still have satisfactory biodegradability. Regardless of the desired degree of branching, there is advantage in being able to carry out an aldol reaction on the oxo product of the hexenes, without need for separating branched aldehyde isomers, and obtain a useful product, particularly considering the low cost nature of the feed-stock and process. The process can be used to obtain a product composed of about 85% 2-pentylnonanol and 15% 2-pentyl-4-methyl-octanol.

30 The oxo process can generally be utilized to achieve 90-95% yields of aldehydes. With linear hexenes as reactant, selectivity to aldehydes without 2-substituents, i.e. α -aldehydoalkanes, can be as high as 60 to 65%, but in large scale

very suitable as a feedstock for producing detergent range alcohols in accord with the present invention.

Particular branched hexene isomers are converted to α -aldehydoalkanes with very high selectivity, with 2-methyl-2-hexene selectivity of 9.2% being obtainable. The mixture of both branched and linear hexenes from propylene dimerization can be converted to α -aldehydoalkanes with selectivity such as about 78%. Thus higher selectivity to aldehydes desirable for the aldol reaction can be obtained by using the crude hexenes mixture for the oxo reaction, rather than only the linear hexenes. Depending upon relative value and availability of the linear and branched hexenes, one might find advantage in using only the branched hexenes in the present process because of the high selectivity in the oxo process to α -aldehydes suitable for aldol reaction.

By use of the entire hexene cut from propylene dimerization in the oxo-aldol process, followed by hydrogenation, a C₁₄ alcohol product can be obtained which is about 15% 2-pentylnonanol, about 10% 2-pentyl-4-methyl-octanol, about 50% 2-pentyl-7-methyloctanol, and about 25% 2(3-methylbutyl)nonanol. If branched C₇ alcohol produced from unreacted aldehyde is dehydrated and recycled to the oxo stage as discussed above, a product can then be obtained which is about 10% 2-pentylnonanol, about 5% 2-pentyl-4-methyloctanol, about 25% 2(4-methylpentyl)-7-methyloctanol, about 10% 2-pentyl-7-methyloctanol, and various multi-branched hexadecanols, e.g., 2(2-ethyl,3-methyl-propyl)-5-ethyl-6-methylheptanol.

As indicated above, the linear content of propylene dimers is fairly low, being around 20% or somewhat higher. At times there may be advantage in separating the linear components for use in the present process, while the branched materials can be used in gasoline with advantage to the octane rating of the gasoline. However, it has been found that the entire hexenes portion of the propylene dimerization product can, if desired, be utilized as feedstock for the present oxo-aldol process. The branched isomers are typified by 2-methyl-2-pentene which, when subjected to oxo reaction with cobalt catalyst, has been found to be very selectively converted to 3-methyl- and 5-methylhexanals. Fortunately it has been found that cobalt catalyst, in contrast to rhodium, has the effect of isomerizing the internal olefins so that the aldehyde group is predominantly on the end of the chain. It appears that the methyl substituent has some influence in directing the oxo reaction to obtain a great predominance of aldehydes with no substituent in the 2-position. It is very important to the use of propylene dimer in the present process, that the oxo product is predominantly an alpha aldehydo-alkane, i.e. there is no substituent in the 2-position. As discussed herein, aldehydes with substituents in the 2-position do not readily undergo aldol reactions. Thus if the internal hexenes were converted largely to such unreacted aldehydes, it would be very difficult to effect self-condensation of such aldehydes to a useful extent, and the use of propylene dimers in the present oxo-aldol process would be impractical. However, as discussed herein, the oxo process with cobalt catalyst converts the hexenes largely to aldehydes which will react in the aldol reaction, making hexenes, obtained from propylene dimerization,

The run was continued for a total of sixteen hours. The measured gas uptake was in very slight excess of theory for hydrogenation of both the olefin and aldehyde groups in the compounds present.

5 The product was filtered through a Celite filter mat to remove catalyst, and the mat was washed with n-hexane. The n-hexane was removed under vacuum, leaving 88 grams of product for distillation. Distillation was carried out at 1333 Pa with 18.1

10 gram being collected at 30-100°C., which gas-chromatography indicated to be 66.4% 2-methylbutanol, 27.5% pentanol, and 4.1% 2-propylheptanol. An additional 38.9 grams was collected at 103.5-105°C., 11.3% 2-propyl-4-methylhexanol and 87.7% 2-propylheptanol.

15 It can be seen that the above described procedure provides 2-propylheptanol with only very minor adulteration by the aldol alcohol product of branched aldehydes. Also the 2-propylheptanol thus produced was readily separated by distillation from the 2-methylbutanol produced by hydrogenation of the 2-methylbutanal which did not undergo the aldol condensation.

20

Exemple 2

n-Pentanal, 246.3 grams, and 2-methylbutanal, 82.1 grams, were mixed and utilized for an aldol reaction, employing 100 ml of aqueous 1 molar sodium hydroxide. The aldehydes were added to the aqueous hydroxide in a flask as described in Example 1. The aldehyde addition took twenty minutes and the mixture was then refluxed, 89-89.5°C., for one hour.

25 Gas chromatographic analysis indicated that 50% of the aldehydes had reacted, and the reaction mixture contained 20.7% 2-methylbutanal, 28.6%

Example 1

An aldol reaction was conducted in a 1 liter round bottom flask equipped with stirrer, addition funnel, reflux condenser and adaptors for nitrogen flow. A 100 ml. amount of aqueous 1 molar potassium hydroxide solution was placed in the flask and heated to about 85°C. n-Pentanal and 2-methylbutanal were admixed in about 3:1 ratio, after each had been purified by distillation, and used for gradual addition to the reaction flask with stirring. Over about one hour, about 300 ml was added containing 187.7 grams n-pentanal and 60.8 grams 2-methylbutanal. The reaction mixture was placed in a separatory funnel; and the lower aqueous phase (87 grams) was separated. The organic layer was washed four times with water, and amounted to 213.5 grams. Gas chromatographic analysis for the starting aldehydes indicated about a 3:1 ratio of 2-methylbutanal to n-pentanal, showing that the n-pentanal had been consumed at a much higher rate in the reaction. The product contained about 70.5% of alkenal condensation product and 25.3% of the starting aldehydes. The product had 2-propylheptanal in about 9:1 ratio to 2-propyl-4-methylhexenal.

A 110.89 gram amount of the product was utilized for hydrogenation, employing 11 grams of cobalt on Kieselguhr catalyst with 4.4. ml H₂O as promoter, in a 300 ml stirred autoclave. The autoclave was pressured to 6.89 MPa with hydrogen and gradually heated, with hydrogen uptake starting at about 40°C. After one hour, the pressure had fallen to 3.31 MPa and the autoclave was again pressured to 6.89 MPa. After two hours, with further addition of hydrogen, the pressure was 10.4 MPa and temperature 160°C.

mixture was washed with sulfuric acid diluted with an equal amount of water, and then with water several times. Distillation was then carried out using a fractionating head, obtaining 44.26 grams at 125 to 5 200°C. at atmospheric pressure, the fraction being 74.1% 2-methyl-1-butanol and 16.3% pentanol, and slightly over 5% C₁₀ alcohols; and then 42.35 grams at 70 to 109°C. at 1330 Pa with 41.8% being 2-propyl-10 4-methyl-1-hexanol and 52.5% 2-propyl-1-heptanol, with less than 2% C₅ alcohols; and 16.6 grams at 109-114 °C. at 1330 Pa with 30.4% 2-propyl-4-methyl-1-hexanol and 66.6% 2-propyl-1-heptanol.

Thus it is demonstrated that the hydrogenated aldol condensation product, viz. 2-propyl-1-heptanol, 15 is produced by hydrogenation of aldol reaction product and separation readily effected from hydrogenated product of unreacted aldehyde, 2-methyl-1-butanol.

Example 4

20 A mixture of butenes was hydroformylated with cobalt catalyst. The reaction was carried out in a 300 ml stirred autoclave in 100 ml. solution with toluene as solvent and 0.3% by weight cobalt carbonyl as catalyst. Utilizing a 5 molar concentration of butenes, with 1-butene and 2-butene in 1:1 ratio and CO:H₂ in 1:1 ratio, the reactor was pressured to 16.64 M Pa and heated to 100°C. and 20.77 M Pa. After 5.2 hours, all but 6% of the olefin had reacted, producing n-pentanal 25 and 2-methylbutanal in 2.0:1 ratio, the pentanal constituting 66.8% of the reaction mixture. The reaction rate was 2.1 gram moles per liter-hour.

pentanal, 4.8% 2-propyl-4-methyl-hexanal and 37.9% 2-propyl-2-heptanal. Thus it is shown that the n-pentanal (valeraldehyde) reacted with itself at a much faster rate than with the 2-methylbutanal, 5 making the 2-propyl-heptanal much more predominant as product than the 3:1 predominance of n-pentanal as starting aldehyde. The lower aqueous phase was removed and the upper organic layer was distilled under vacuum. Volatile materials, including water, 10 n-pentanal, 2-methylbutanal, and pentanol, were removed under vacuum reaching 2666 Pa a total of 78 grams being collected in cold traps. Heat was then applied and 3.88 grams collected at a head temperature of 52-86°C, 9.93 grams at 86°C., 5.65 15 grams at 90°C., and an additional 26.04 grams at 90°C. All of the fractions were predominantly 2-propyl-2-heptanal, in the range of about 70 to 80%, with 2-propyl-4-methyl-hexenal constituting only a small fraction of the product. The unreacted 20 2-methylbutanal was, as indicated, readily separated from the much higher boiling 2-propyl-2-heptanal product.

Example 3

An aldol product mixture was utilized for hydrogenation. The product mixture was from 25 reaction of n-pentanal and 2-methylbutanal, with the latter being in excess during much of the reaction and contained about 54% 2-propyl-2-heptanal and 2-propyl-4-methyl-2-hexenal in about 3:2 ratio. The hydrogenation was conducted with cobalt on 30 kieselguhr at pressures up to about 10.3 MPa and temperatures from 125 to 160°C. for three and one-half hours. The product was vacuum filtered and the filter washed with hexane which was removed by vacuum. Chromatography indicated the mixture was 35 about 35% C₅ alcohols and 60% C_{7,8} alcohols. The

Table 1

Plasticizer (40% in PVC)	Low Temp. Flex (T_f) *	Volatility	
		1 day	6 days
Di(2-propylheptyl) phthalate	-40°C	1.0%	3.7%
5 Dioctyl phthalate (2-ethylhexyl)	-39°C	3.9%	19.0%
Diisononyl phthalate	-36°C	1.8%	7.0%
Diisodecyl phthalate	-37°C	1.2%	4.2%

*Determined in a standard Clash-Berg test.

10 It is recognized in the Plastics Industry that the more efficient a plasticizer is, the lower the temperature in the Clash-Berg low temperature flexibility test, i.e. a T_f of -45°C. indicates a far superior plasticizer than a T_f of -35°C. Therefore
15 in the above table it can be seen that the propylheptyl phthalate compares favorably, having a lower flexibility temperature, as well as appreciably lower volatility compared to dioctyl phthalate. An additional factor which is advantageous in the product prepared
20 by the present procedure is the fact that adulteration with branched aldehyde can be tolerated. Thus 2-propyl-4-methyl-hexyl phthalate has a low temperature flexibility value of -31.5, and the presence of 12% or so of this in the phthalate will only raise the low
25 temperature flexibility, to about -38.5°, and the volatility is still excellent. By contrast dioctyl-phthalate would be more sensitive to adulteration by isomers as di(2-ethyl-4-methylpentyl) phthalate has a low temperature flexibility (T_f) of -30°C and a very
30 high volatility (6.7% in 1 day test.)

Example 5

A hydroformylation similar to Example 4 was conducted utilizing a 1-butene to 2-butene ratio of 1:2 and obtaining a n-pentanal to 2-methylbutanal ratio of 3.2 after 1 hour and 3.1 after 6-hours.

5 In similar procedures, the ratio was in the range of 2.8:1 to 3.1:1.

Example 6

The procedure of Example 4 was repeated but utilizing 2-butene as the olefin, to obtain a pentanal to methylbutanal ratio of 71:29 at 100°C., 10 and 69:31 at 110°C.

Example 7

A mixture of butenes, 1-butene:2-butene:isobutylene in 1:1:2 ratio, was hydroformylated in accord with the procedure of Example 4, producing pentanal:2-methylbutanal:3-methylbutanal in 15:5.2:11 ratio after one hour reaction.

The hydroformylations of butenes take place at excellent rates over cobalt catalysts and with good selectivity to aldehydes, selectivities greater than 93% being obtainable. With butene-2 as the 20 substrate and 0.3 wt. % cobalt, (based on cobalt metal) rates over 5 gram moles per liter-hour have been observed at 110°C.

A sample of 2-propylheptanol was used to esterify phthalic acid to obtain a plasticizer. 25 The plasticizer was used to plasticize polyvinyl chloride (PVC) and found to have good plasticizing properties, as compared with other plasticizers in Table 1.

alcohols was separated by distillation and the C₁₀ alcohol was converted to its phthalate ester for use as a plasticizer.

Example 10

5 Dimerization of propylene over transition metal catalysts produces a mixture of hexenes.

10 The linear hexenes in the mixture can be separated and such linear hexenes are for the most part 2-hexenes. The following procedure illustrates the reaction of 2-hexenes in an oxo reaction, followed by an aldol reaction of the product. A sample of refinery 2-hexenes was passed through basic alumina particles for removal of oxides and 802 grams of the hexenes was placed in a 1 gallon stainless steel autoclave with 15 4.75 grams Co₂(CO)₈ catalyst. The autoclave was pressured to 16.64 M Pa with 1:1 carbon monoxide and hydrogen, and heated to 110°C. The temperature was kept at about 110°C for 3 hour and then rose to about 130° as the procedure was continued for about 20 5 hours. A 916.5 gram product was obtained, with conversion about 94% with about 78% selectivity to C₇ compounds, and 71.5% to C₇ aldehydes. Chromatography indicated the aldehydes were in ratio of about 29.4 n-heptanal to 16.7 2-methylhexanal to 25 8.5 2-ethylpentanal. A 907 gram amount of the product was distilled, with a final pot temperature of 120°C. and vacuum of 400 Pa to obtain a 608 gram distillation fraction and 278 gram residue. Chromatography indicated the fraction included C₇ 30 aldehydes in ratio 33.4 n-heptanal to 26.8 2-methylhexanal to 17.2 2-ethylpentanal, and minor amounts of other components. Evidently there was more loss of the normal aldehyde than the branched ones in the distillation.

Example 8

A phthalate plasticizer was prepared by using an alcohol mixture for esterification composed of 85% 2-propylheptanol, 11% 2-propyl-4-methylhexanol, and 4% 2-propyl-5-methylhexanol. The alcohol mixture was prepared in accord with procedures described herein, involving an aldol reaction of 75% n-pentanal, 25% 2-methylbutanal and 2% 3-methylbutanal, as obtainable from oxo reaction of butenes having a very small isobutylene content. The plasticizer with polyvinyl chloride (40% plasticizer) gave a low temperature flexibility (T_f) value of -38 to -39, 1 day volatility of 1.2% and 6-day volatility of 4.1-4.3%.

Example 9

A mixture of 709 gm of n-pentanal, 237 gm of 2-methylbutanal and 19 gm of 3-methylbutanal was added over 40 minutes with stirring, to 300 ml of 1 molar potassium hydroxide solution at 88°C. After the addition was completed, the reaction mixture was maintained at 88°C with stirring for a further 20 hours, at which time the n-pentanal was 96% converted. The aldol product consisted of 83% 2-propylheptanal, 13% 2-propyl-4-methylhexenal and 4% 2-propyl-5-methylhexenal. The reaction mixture also contained 75% of the originally charged 2-methylbutanal.

The reaction product was cooled and the organic phase was separated and hydrogenated at 160°C under 10.33 MPa of hydrogen pressure in the presence of a cobalt on kieselguhr catalyst. The hydrogenation of the enals produced the corresponding alkenols, and the resulting mixture of C₅ alcohols and C₁₀

by distillation, with a 280 gram fraction being obtained at 110-115°C. at 266 Pa from 1180 grams of hydrogenation product. The fraction was in large predominance composed of C₁₄ alcohols.

5

Example 11

A mixture of hexenes produced by the Dimersol^R dimerization process was utilized as olefin reactant. The crude hexene cut from the dimerization was used, and had the distribution of linear and branched 10 hexenes typical of such material. A 1029 gram amount of the hexenes was used in a 3.8 liter autoclave with 6.04 grams catalyst, Co₂(CO)₈, 0.02 weight %. Peroxides had been removed from the hexenes by treatment on a basic alumina column. The autoclave was 15 taken to reaction conditions with 1:1 CO/H₂ and maintained at 110°C. and 18.0 M Pa for 9 hours, with 80% of theoretical gas uptake, and then continued overnight. Chromatography indicated high conversion to C₇ aldehydes, with minor amounts of 20 residual hexenes. A 1360 gram amount of the product was subjected to distillation, with a 797 gram fraction being obtained at pot temperatures of 60 to 97°C. as the vacuum dropped from 11.97 K Pa to .66 K Pa. Chromatography indicated a high proportion 25 of C₇ aldehydes with a very small amount of C₆ olefins.

A 792 gram amount of the above aldehyde fraction was utilized in an aldol reaction, adding the aldehyde material from an addition funnel to a 30 reaction flask containing 564 grams methanol and 250.9 grams 0.8 molar sodium hydroxide. The addition took about 6 hours, with stirring at about 500 rpm and temperature at 72-73°C. The reaction mixture was then refluxed for 1.5 hours.

It is feasible to achieve a higher percentage of n-aldehyde than present in the above distillation fraction, such as 60% or better, and therefore n-heptanal was added to the above fraction to have a more typical aldehyde for aldol reaction, about 600 grams of the above fraction being used with 500 grams n-heptanal. A 300 ml amount of 0.8 molar sodium hydroxide was placed in a reaction flask with 955 ml methanol, and the aldehydes were placed in an addition funnel. The reaction medium was heated to about 71°C., and addition was slowly started and completed in about 13 hours. Chromatography indicated about 50% completion of the reaction, with C₁₄ aldehydes in ratio of about 23.4% 2-pentynon-2-enal to 8.72% 2-pentyl-4-methyloct-2-enal to 1.4% 2-pentyl-4-ethylhept-2-enal. Several C₇ aldehydes were also present in the ratio of 22.9 heptanal to 8.5 2-methylhexanal to 5.3 2-ethylpentanal.

The aldol condensation product was hydrogenated over a cobalt/kieselguhr catalyst, using 131 grams catalyst with 1336 grams of the condensation product. The materials were maintained at about 160°C. and 10.43 M Pa of hydrogen for about two hours when reaction appeared complete. Reaction conditions were maintained for an additional 4.5 hours. Analysis indicated about 99% completion of the hydrogenation. The product contained 2-pentynonanol in about 18.4 to 7.2 ratio to a mixture of 2-pentyl-5-methyl-octanol and 2-pentyl-4-ethylheptanol and large amounts of C₇ alcohols from the unreacted aldehyde, being heptanol in a 27.5 to 16.3 ratio to a mixture of 2-methylhexanol and 2-ethylpentanol. The product was fractionated

filtered to remove catalyst, and the filtrate was distilled. The process produced several C₁₄ alcohols in very substantial amounts, with a number of others in very small amounts. Several C₇ alcohols from 5 unreacted aldehyde were also present in substantial amount.

The examples of procedures for converting propylene dimers, via oxo, aldol and hydrogenation, to C₁₄ alcohols, illustrate that the reaction is 10 feasible, although conditions in the procedures are not optimized and results better than those reported can be achieved by appropriate determination of conditions. In the procedures it was found that 15 a co-solvent, which can be referred to as a phase transfer solvent, such as a hexane diol, resulted in higher conversion in the aldol reaction than was obtained by the use of methanol. The diol apparently aids by providing greater solubility of the aldehyde reactants in catalyst-containing phase, thereby 20 permitting more complete reaction. Other diols exhibiting appreciable solubility for both the reactants and aqueous catalyst system are expected to be similarly useful, and appropriate usage of such systems should make it possible to greatly 25 exceed the 63% or so conversion obtained above, particularly when the aldehyde reactants contain very high proportions of aldehydes free of 2-substitution, as can be obtained by oxo reaction of 30 the complete hexenes mixture obtained by propylene dimerization.

The hexenes product from a Dimersol[®] dimerization refinery product was analyzed and found to have the following distribution.

Analysis of a sample indicated only about 1 part aldol product to 3 parts aldehyde, on a mole basis. The reaction was continued at reflux overnight, giving 1 part aldol product to about 2.6 parts 5 aldehyde reactant. During the reaction it was observed that the reaction mixture had a large upper phase and a smaller lower phase, indicating that methanol was not very effective in promoting miscibility and reaction, possibly because of the relatively long chain length of C₇ aldehydes. Chromatography showed a fair amount of the C₁₄ aldol 10 product, including 2-pentynonenal, and a large amount of unreacted C₇ aldehydes.

The above aldol product was subjected to 15 further aldol reaction, after removing the methanol to employ different conditions. A 552 gram amount of the aldol condensate, 55.6 area percent C₇ aldehydes and 31.5 area percent C₁₄ enals, was placed in an addition funnel and added to a reaction 20 flask containing 163 grams 0.8M NaOH and 389 grams 2,5-hexanediol. Addition was complete after 45 minutes, with temperature maintained at 100°C. with agitation of the reaction mixture. The reaction mixture was then refluxed at 100°C for 25 1.75 hours. The reaction mixture separated into upper and lower phases of about equal weight. The conversion had been improved in that the ratio of C₁₄ enals to C₇ aldehydes in the product (upper phase) was now about 1.7 to 1.

30 A 515 gram amount of the product was subjected to hydrogenation, employing 51.65 grams cobalt/kieselguhr catalyst and 160°C., about 10.98 M Pa 35 hydrogen. Approximately 549 grams of product was recovered. The conversion of C₁₄ enals to C₁₄ saturated alcohols was about 90%, with about 10% found as unsaturated alcohols. The product was

Dimersol® dimerization process product and various hexene components thereof were reacted in an oxo variation over cobalt catalyst generally as described in Examples herein. The product distribution obtained are reported in Table 2 below, along with the reaction temperatures and times. The D-Mixture in the table is the mixture of all the hexenes obtained in the Dimersol dimerization process. The particular aldehydes are identified below the table by key to Roman numerals with the aldehyde group in all cases in the 1-position. The % aldolable product as reported includes all aldehyde products except those with 2-substituents.

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Hexene Distribution

% (100% Basis)

2,3-dimethyl-2-butene	6.4
2-methyl-2-pentene	39.2
trans-4-methyl-2-pentene	15.9
cis-4-methyl-2-pentene	2.9
2-methyl-1-pentene	5.0
2,3-dimethyl-1-butene+4-methyl pentene	1.7
trans-2-hexene	16.5
trans-3-hexene	5.8
cis 3 + cis 2-hexene	5.6
1-hexene	1.0

28.9

It will be noted that, despite the branching in the dimerization product mixture, very high selectivities to "aldolable" aldehydes are obtained, such as better than 75%. The result is even more pronounced when individual branched olefins are reacted, even when the methyl branches are located on an unsaturated carbon atom. Use of a catalyst which permits migration of the double bond, as the cobalt catalysts herein, is essential to this result.

10 One of the components found in the dimerization product mixture, 2,3-dimethyl-2-butene, is relatively unreactive in the oxo reaction, so, if desired the reaction can be effected to leave it unreacted.

15 With further regard to the aldehydes obtained by oxo reaction of propylene dimerization product, one of the isomers present in large amount is 3-methylhexanal. This aldehyde reacts readily in the aldol condensation. Moreover, in cross-aldol with n-heptanal, it appears to exhibit a very strong 20 preference for the condensation to occur on the 2-carbon of the normal aldehyde, i.e. to produce 2-pentyl-5-methyloctanal, rather than 2(1-methylbutyl)nonanal. The latter compound, having adjacent methyl substituents, might be more resistant to biodegradation when converted to a detergent alcohol. 25 The 5-methylhexanal, also obtained in substantial amounts, apparently reacts readily in an aldol reaction to give suitable product.

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Table 2
Oxo Product Distribution

Hexene	Temp. (°C)	Run (hours)	%						IX Aldolable ^a	
			I	II	III	IV	V	VI	VII	
D-Mixture	110	23	15.3	19.4	8.7	39.1	4.4	3.1	1.4	7.5
D-Mixture	130	4	14.9	25.0	8.5	36.2	4.3	1.8	1.1	7.4
" "	3	15.4	23.5	8.8	37.9	4.5	0.7	1.1	7.5	0.7
" "	2	16.8	25.5	9.6	33.8	4.9	0.8	1.0	7.2	0.6
" "	1	18.8	24.5	10.7	31.8	5.4	trace	1.4	6.8	0.5
2-methyl-2-pentene	116	3	-	34.3	-	56.6	-	-	1.3	6.9
2-methyl-2-pentene	130	3	-	33.6	-	56.6	-	-	1.4	7.2
2-methyl-1-pentene	116	3	-	10.6	-	84.4	-	-	0.4	2.5
4-methyl-2-pentene	130	3	-	65.9	-	17.3	-	trace	1.6	15.3
	2	-	65.1	-	16.6	-	-	1.6	16.8	trace
	1	-	67.6	-	14.2	-	-	1.4	16.8	trace
										81.8

I = heptane
II = 5-methylhexane
III = 2-methylhexane
IV = 3-methylhexane
V = 2-ethylpentane

VI = 3,4-dimethylpentane
VII = 2-ethyl-3-methylbutane
VIII = 2,4-dimethylpentane
IX = 2,2-dimethylpentane

It has also been found that pentenes can be hydroformylated to hexanals, and the hexanals condensed in an aldol reaction and hydrogenated to form 12-carbon alcohols, in a manner similar to 5 such reactions with the hexenes.

The processes herein can employ various olefins as starting material and the conditions of the various oxo, aldol etc. stages as described for butenes are generally applicable to the processes 10 employing hexenes or other olefins as starting material. With particular reference to the oxo stage, it will be noted that cobalt catalyst is employed with the hexenes in order to promote migration of the olefinic bond and high selectivity 15 to desired aldehyde isomers, such catalysts being for example $\text{Co}_2(\text{CO})_8$ which may be equivalent to $\text{HCo}(\text{CO})_4$ under reaction conditions, and $\text{HCo}(\text{CO})_3$ (Phosphine ligand).

The C_{14} or other detergent range alcohols 20 produced by the present process can be readily converted to detergents by known procedures. Thus non-ionic detergents are prepared by reaction with ethylene oxide to have a desired number of ethoxyl groups, e.g. 6 to 10 or 12 or so. These, or other 25 ethoxylated alcohol, possibly with 2 to 3 ethoxyl groups can be reacted to form an alcohol ether sulfate, having a sulfate anionic end group with a sodium or other cation. The alcohols can also be reacted to prepare sulfate derivatives. The 30 detergents thus prepared will have the requisite hydrophobic groups for detergent properties. Moreover, the structures are such as to provide biodegradability, in that the structures are acyclic

The Dimersol[®] dimerization process has been referred to in various publications, e.g. see "How First Dimersol is Working" by Benedek et al, Hydrocarbon Processing, May 1980, page 143; also Chauvin et al, "The IFP Dimersol[®] Process for the Dimerization of C₃ and C₄ Olefinic Cuts", Advances in Petrochemical Technology, presented at American Institute of Chemical Engineers, April 13, 1976, Kansas City, Missouri

The combination of the Dimersol[®] dimerization process, oxo process, aldol and hydrogenation 10 provides a very efficient route from propylenes to detergent range alcohols. One of the known routes to such alcohols relies upon oligomerization of ethylene to obtain higher molecular weight materials which are then subjected to an oxo reaction. The 15 presently proposed route is in many respects more efficient and economical than those involving ethylene oligomerization, as propylene costs less than ethylene, and the reactions involved using dimerization, oxo and aldol are more straight forward than an 20 oligomerization which can produce a broad mixture of products and require extensive equipment and procedures to direct it to suitable product. As discussed hereinabove, the mixture of isomers obtained from a dimerization can be carried through 25 the oxo, aldol and hydrogenation reactions to obtain high overall conversions and yields, despite the presence of extensive branching in the materials. It is fortunate to find that a high proportion of the materials are capable of taking part sequentially 30 in all of the required reactions, and in particular that the aldehyde failing to react in the aldol reaction, because of 2-substitution, is at a comparatively low level.

Example 12

A freshly distilled sample of 2-pentene was hydroformylated in a 300 ml autoclave, employing 0.41 gram $\text{Co}(\text{CO})_8$ catalyst with 65.84 grams pentene. A 1:1 mixture of CO/H_2 was used, with initial charge to 10.43 MPa and heating to 120°C. and 20.67 MPa with agitation at 1000 rpm. Gas uptake was observed, as the pressure was increased to 20.67 MPa. After about 2 hours, an 83 gram product was obtained. Chromatography showed a small residual amount of pentene and C_6 aldehydes in the ratio of 61.1 hexanal to 28.9 2-methylpentanal to 10.0 2-ethylbutanal. An aldehyde sample was provided to have aldehydes in the same ratio, using 189.1 grams hexanal, 89.9 grams 2-methylpentanal, and 31 grams 2-ethylbutanal, and placed in an addition funnel for addition to 110 ml of 0.8 M NaOH in a round bottom flask equipped with a mechanical stirrer. Heating was begun and addition was started after about 15 minutes and continued as reflux started around 91°C. Addition was completed in about 40 minutes. Stirring was continued for an hour, but without further heating, and a sample was taken. Analysis indicated partial reaction. The reaction mixture was heated to 95°C. for an additional 1 1/2 hours. Upper and lower phases of the reaction mixture were separated, and the upper phase was analyzed. The analysis indicated better than 25% conversion to C_{12} enal, nearly all being 2-butyloctenal, and large amounts of unreacted C_6 aldehydes, the major part of which was branched aldehydes. The aldehyde mixture can readily be hydrogenated to the corresponding alcohols.

alkyl groups which are essentially free of any tertiary carbon groups and in which branching on adjacent carbon atoms is absent or at a very low level. The common 2-branching characteristic of aldol product, with or without various additional methyl or other lower alkyl branches in non-adjacent positions, is not expected to have any important effect on the biodegradable nature of the compounds. An alcohol ether sulfate prepared from 2-pentylnonanol has been described as biodegradable by Cranland et al, Surfactant Congress No. 4, Vol. 1, page 93 (1967). Also Kravetz et al, Proceedings of the American Oil Chemists' Society, 69th annual meeting, May, 1978, St. Louis, Mo., concluded that variation of branching from 45% to 75% linear had no appreciable effect on biodegradation rates of primary alcohol ethoxylates, and make reference to 58% branching giving biodegradation at rates not appreciably different from zero branching. It is further of interest that Farnesol, a natural alcohol with branching, degrades somewhat slower than a straight chain alcohol, but still degrades at a rate sufficient to meet stringent biodegradability requirements. Farnesol is a 15 carbon alcohol with methyl branches at the 3, 7 and 11 positions.

together, rather than adding the n-aldehyde to the branched aldehydes in the reaction mixture as in the foregoing procedure. The phase transfer catalyst was effective in improving conversion in this procedure, but use of co-solvents, such as methanol or diols, may be more practical for large scale continuous operations. The use of hexanediol has been shown effective for aldol reaction of heptanals herein, and can similarly be used with hexanals.

It will be noted that the alcohols produced from both the pentenes and hexenes feedstocks are intended for use as detergent range alcohols. The considerations herein as to reaction conditions and various parameters of the oxo and aldol reactions as described for the hexenes and resulting C₇ aldehydes also are in general applicable to the pentenes and resulting C₆ aldehydes. The C₁₂ alcohols produced from the reactions starting with pentenes will have the hydrophobic groups such alcohols provide in detergents, and the groups will have a degree of branching similar to that of C₁₄ alcohols from hexenes. It is feasible to substantially avoid presence of branches on adjacent carbon atoms. In one particular aspect the present invention is directed to a process of preparing alcohols from an oxo reaction with olefins selected from those having 5 to 6 carbon atoms, or mixtures thereof, to obtain aldehydes having 6 to 7 carbon atoms, comprising high amounts of α -aldehydoalkanes, and effecting aldol conversion with limited participation of 2-substituted aldehyde to obtain aldol product, which is then hydrogenated to C₁₂ or C₁₄ alcohols having properties valuable for use in detergents.

Exemple 13

An aldol procedure was carried out as in Example 12, except that the amount of water was increased ten fold. The same amount of NaOH was present, although now in much more dilute solution. Because of the large volume, less effective stirring was achieved. After a two hour reaction, analysis indicated substantial conversion to C₁₂ enals, although somewhat lower than in Example 12.

10

Example 14

An aldol reaction was carried out as in Example 12, employing 6.1 to 2.9 to 1 ratio of hexanal to 2-methylpentanal to 2-ethylbutanal, the total amount being 310 grams. The branched aldehydes were placed in a flask with 110 ml of 0.8 M NaOH, and tetrabutylammonium chloride in an amount molecularly equivalent to the NaOH. The tetrabutyl-ammonium chloride serves as a phase transfer catalyst. The reaction flask was heated to reflux and addition was started. The addition continued for about 6 hours with reflux temperatures (pot) from 90-95°C. The mixture was cooled and separated into two phases. Analysis of the upper phase showed better than 75% conversion to C₁₂ enals, about half of which was 2-butyloctenal, and the remainder mainly a mixture of 2-buty1-4-ethylheptenal and 2-buty1-4-ethylhexenal. In the unreacted C₆ aldehydes present, the branched aldehydes were in greater amount than the hexanal. The reaction can be directed to produce a higher percentage of product from the n-hexanal by adding the aldehydes

6. A method of preparing ten-carbon plasticizer alcohols which comprises conducting an oxo reaction at temperatures in the range of 80 to 150°C. and pressures sufficient to maintain catalyst stability but not over 34.5 M Pa with mixed butenes and hydrogen and carbon monoxide to obtain amyl aldehydes with at least about 66% n-pentanal content, and subjecting the amyl aldehyde mixture to an aldol reaction in aqueous alkaline medium at temperatures of 60° to 150°C. to cause at least about 80% conversion to aldol products comprising at least about 80% of the aldol product of n-pentaldehyde and no more than 20% of cross aldol product of n-pentanal with other aldehydes, hydro- generating to alcohols to obtain mainly 2-propylheptanol 15 along with 2-propyl-4-methylhexanol and 2-methylbutanol and separating the alcohols from the reaction mixture, obtaining a ten-carbon atom plasticizer alcohol containing at least about 80% 2-propylheptanol and adapted to contribute good plasticizer properties to a phthalate 20 diester prepared therefrom.

7. A process of preparing a plasticizer alcohol comprised of 2-propylheptanol and no more than 15% of 2-propyl-4-methylhexanol which comprises conducting an oxo reaction at temperatures in the range of 5- 80 to 150°C. and pressures sufficient to maintain catalyst stability but not over 34.5 M Pa with a mixture of normal butenes and hydrogen and carbon monoxide to obtain a mixture of amyl aldehydes with at least about 66% n-pentanal content and without separation of 10 aldehyde isomers conducting an aldol reaction in aqueous alkaline medium at temperatures of 60° to 150°C. of the mixture to convert a high percentage of such aldehydes to ten-carbon aldol products but stopping the reaction short of complete conversion so that 15 substantially all of the n-pentanal has formed aldol product but a portion of the branched aldehyde in

WHAT IS CLAIMED IS:

1. A process of preparing alcohols which comprises conducting an oxo reaction with olefins selected from those having from 3 to 7 carbon atoms to obtain aldehydes having from 4 to 8 carbon atoms and comprised of at least 50% α -aldehydoalkanes and subjecting the aldehydes to an aldol reaction to cause good conversion of the aldehydes to aldol product but with that produced from cross-aldol of 2-substituted aldehydes constituting no more than 20% of the product, and hydrogenating to obtain alcohols.
2. The process of Claim 1 in which the aldehydes have α -aldehydoalkane content of from about 60 to about 80% and the conversions of aldehyde to aldol product are in the range of about 75% to about 90%.
3. The process of Claim 1 in which the conversion of aldehyde other than 2-substituted aldehyde in the aldol reaction is at least about 95%.
4. The process of Claim 1 in which the oxo reaction is conducted with hydrogen and carbon monoxide at temperatures in the range of 80 to 150°C. and pressures sufficient to maintain catalyst stability but not over 34.5 M Pa, and the aldol reaction is conducted in aqueous alkaline medium at temperatures of 60 to 150°C.
5. The process of Claim 4 in which a cobalt catalyst is employed for the oxo reaction.

12. The method of Claim 9 in which substantially linear butenes which are at least one-third 1-butene are hydroformylated by reaction with carbon monoxide and hydrogen over cobalt catalyst at temperatures of about 80° to about 150°C. to obtain amyl aldehydes with n-pentanal: 2-methylbutanal ratios in the range of about 2.8:1 to 3.1:1, and the aldehydes are subjected to aldol reaction in the presence of aqueous alkali hydroxide, constituting about 15% to 75% by volume of the aqueous alkali and aldehyde reactant, at temperatures of about 90° to about 130°C. to condense nearly all of the n-pentanal while leaving some 2-methylbutanal unreacted to obtain ten-carbon enals with at least about 85% from self-condensation of n-pentanal, followed by hydrogenating over hydrogenation catalyst with hydrogen at elevated pressure to obtain alcohols by reduction of enals and remaining amyl aldehydes, the ten-carbon alcohols obtained being composed of about 85 to 95% 2-propylheptanol, and separating five-carbon alcohols and 10-carbon alcohols by distillation.

13. The process of preparing aldol products which comprises subjecting an amyl aldehyde mixture containing at least about 70% n-pentanal and a substantial amount of 2-methylbutanal to an aldol reaction with strong alkaline catalyst at temperatures of 90 to 130°C. to cause substantially all of the n-pentanaldehyde to react, stopping the reaction with unconverted 2-methylbutanal still present and producing ten-carbon enals composed of at least about 85% 2-propylheptenal.

14. The process of Claim 12 in which the hydrogenation is conducted at pressures above 3.45 MPa and temperatures above about 130°C.

the aldehyde mixture is not reacted, hydrogenating the resulting aldehyde mixture and obtaining a 2-propylheptanol product in which the 2-propyl-4-methylhexanol co-product constitutes no more than 20 about 15% of the 10-carbon alcohol composition, in admixture with 2-methylbutanol.

8. The process of Claim 7 in which the 2-propyl-4-methylhexanol constitutes about 11-12%.

9. The process of preparing ten-carbon plasticizer alcohols which comprises conducting an oxo reaction at temperatures in the range of 80 to 150°C. and pressures sufficient to maintain catalyst 5 stability but not over 34.5 MPa of normal butenes and hydrogen and carbon monoxide to obtain aldehydes which are at least about 70% n-pentanal and subjecting the aldehydes to an aldol reaction in aqueous alkali of about 1 to 10% concentration by weight to 10 cause nearly all of the n-pentanal to be condensed, producing ten-carbon enals comprised of at least about 85% of 2-propylheptenal, and hydrogenating the 10-carbon enals to obtain alcohols comprised of at least about 85% 2-propylheptanol, and a substantial 15 portion up to about 15% of other ten-carbon atom isomeric alcohols.

10. The process of Claim 9 in which the oxo process is conducted at 6.89 to 27.56 MPa in the presence of cobalt catalyst, and the aldol reaction is conducted at about 90° to about 130°C.

11. The process of Claim 9 in which the amyl aldehydes are comprised of 70 to 85% n-pentanal and the ten-carbon alcohols are 85 to 95% 2-propylheptanol.

15. A process of preparing alcohols which comprises conducting an oxo reaction with a hexene mixture comprised mainly of methylpentanes with no more than 30% linear hexenes, and obtaining C₇ aldehydes with less than 30% 2-substituted aldehydes, subjecting the aldehydes to an aldol reaction to obtain aldol product with conversion of at least 70% and hydrogenating to obtain alcohols.

16. The process of Claim 15 in which no more than one-third of the 2-substituted aldehydes are converted to aldol product.

17. The process of Claim 15 in which the hexene mixture comprises substantially the hexenes mixture from a dimerization of propylene over a nickel and aluminum alkyl catalyst.

18. The process of Claim 15 in which C₁₄ alcohols are produced with 2-pentyl-7-methyloctanol being the isomer present in largest amount.

19. The process of Claim 15 in which more than 75% of the C₁₄ alcohol product has double branching but has practically no branches located on adjacent carbon atoms.

20. The process of Claim 15 in which the oxo reaction is conducted with cobalt catalyst and hydrogen and carbon monoxide at temperatures in the range of 80° to 150°C. and pressures sufficient to maintain catalyst stability but not over 34.5 MPa and the aldol reaction is conducted in aqueous alkaline medium at temperatures of 60° to 150°C.

21. The process of preparing alcohols in which substantially linear hexenes are separated from a propylene dimerization mixture and subjected to an oxo reaction to obtain better than 50% selectivity to α -aldehydoalkanes and subjecting the oxo reaction product to an aldol reaction to produce an aldol product with no more than about 15% content from cross aldol of 2-substituted aldehydes, and hydrogenating to produce alcohols.

22. The process of Claim 21 in which the product contains at least 85% 2-pentynonanol and no more than about 15% 2-pentyl-4-methyloctanol.

23. The process of preparing aldol products which comprises subjecting a C₇ aldehyde mixture comprising at least 50% methylhexanals but no more than 30% of 2-substituted aldehydes to an aldol reaction with strong alkaline catalyst to effect high conversion of the methylhexanals to aldol product but with no more than one-half of the 2-substituted aldehydes being converted to aldol product.